



Short communication

Electrical conduction in dense Mg^{2+} -doped SnP_2O_7 – SnO_2 composite ceramic for intermediate temperature fuel cellHongtao Wang^{a,b}, Dongmei Zhao^a, Zuolong Ding^a, Xuli Deng^a, Guilin Ma^{a,*}, Zhufa Zhou^{a,*}^a Key Laboratory of Organic Synthesis of Jiangsu Province, College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, China^b College of Chemistry and Chemical Engineering, Fuyang Teachers College, Fuyang 236041, China

H I G H L I G H T S

- Dense Mg^{2+} -doped SnP_2O_7 – SnO_2 composite ceramic was prepared at 600 °C.
- SEM image indicated that the composite ceramic is very dense.
- The H_2 /air fuel cell generated the maximum power density of 93.71 mW cm^{-2} at 250 °C.

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A novel dense Mg^{2+} -doped SnP_2O_7 – SnO_2 composite ceramic (5 mol % Mg^{2+}) was prepared through an effective preparation method. The composite phases of SnO_2 and SnP_2O_7 in the ceramic were determined by XRD method. The result of SEM image indicated that the composite ceramic is very dense. The H_2 /air fuel cell using the sample as an electrolyte generated the maximum power densities of 39.69 mW cm^{-2} at 150 °C, 66.89 mW cm^{-2} at 200 °C and 93.71 mW cm^{-2} at 250 °C, respectively. The result indicated that Mg^{2+} -doped SnP_2O_7 – SnO_2 composite ceramic is a promising solid electrolyte for intermediate temperature fuel cells.

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1. Introduction

Some ABO_3 perovskite-type oxides, e.g. BaCeO_3 , SrCeO_3 doped with some acceptor dopants for B-site showed protonic conduction under hydrogen-containing atmosphere at elevated temperatures, and they would be applied for various hydrogen energy systems such as hydrogen pump, high temperature fuel cells (HTFCs) and hydrogen sensors, etc. [1–5]. However, for practical applications, the sealing and bonding materials for HTFCs are required to have high and sustainable stability at elevated temperatures. In order to decrease the working temperature, expand the material selectivity and improve the stability and reliability of the system, developing the electrolyte materials able to work at intermediate temperatures below 700 °C has been promoted [6–8]. Recently, intensive focus has been given to SnP_2O_7 -based materials due to their high electrical conductivity and potential applications in intermediate

temperature electrochemical devices including fuel cells, gas sensors and so on. [9–18]. However, it should be kept in mind that the samples in the previous studies were prepared by merely pressing SnP_2O_7 -based powders into pellets and the relative densities were much lower than traditional ceramics, e.g. YSZ, doped CeO_2 , etc. In order to enhance electrical conduction and application performances, it is necessary to increase relative density of SnP_2O_7 -based materials through adopting more effective preparation methods. Hibino et al. reported that inorganic–organic composite membranes exhibited well cell performances from 100 to 250 °C [19–21]. Until now, only a few papers dealt with the preparation of SnP_2O_7 -based ceramic pellets through sintering procedure above 900 °C [22–25]. Unfortunately, the conductivities of the ceramic pellets were several orders of magnitude lower than the previously reported conductivities of the pellets prepared merely by pressing powders. It may be speculated that the preparation temperatures of the ceramic pellets were so high that some amount of $\text{P}_2\text{O}_7^{4-}$ ions in the samples would lose by the vaporization of phosphorus species during the preparation process, thus

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resulting in decrease of the conductivities [9]. Recently, Hibino et al. prepared dense SnP_2O_7 – SnO_2 composite ceramics, which exhibited relatively high proton conductivities in the temperature range of 100–600 °C [26,27]. Hibino et al. also reported that the overall conductivity of Mg^{2+} -doped SnP_2O_7 , which was prepared by only pressing powders into pellets, increased with increasing Mg^{2+} doping level [28]. Therefore, it is interesting to investigate the Mg^{2+} -doped SnP_2O_7 – SnO_2 composite ceramics. Nisiro et al. reported that the densification of SnO_2 was greatly improved by doping 2 wt% CuO as a sintering aid since the forming of liquid-phase eutectic CuO – Cu_2O in the sintering process would remarkably promote the sinterability [29]. In this study, a novel dense Mg^{2+} -doped SnP_2O_7 – SnO_2 composite ceramic (5 mol % Mg^{2+}) was prepared with CuO as a sintering aid. A hydrogen–air fuel cell using the composite ceramic as an electrolyte was constructed and the cell performances were also explored.

2. Experimental

The Mg^{2+} -doped SnP_2O_7 – SnO_2 composite ceramic (5 mol % Mg^{2+}) was prepared through the manner similar to that reported by Shen [26] and Sato et al. [27]: a porous 5 mol % Mg^{2+} -doped SnO_2 substrate was first prepared and then reacted with 85% H_3PO_4 solution at elevated temperature. The required amounts of SnO_2 (Luoyang Ship Material Research Institute, 50–70 nm), MgO (99.9%) and additional 1.5 mol % CuO as a sintering aid [29] were fully mixed. The mixture was ground in ethanol medium using a planetary ball mill machine with an agate mill container and agate balls at 150 rpm for 6 h and dried by infrared lamp. To form sufficient porosity in the Mg^{2+} -doped SnO_2 substrate, 10 wt% starch was added as the pore former. The well mixed powder was pressed into pellet under 70 MPa, and subsequently fired at 1150 °C in air for 5 h. The obtained porous Mg^{2+} -doped SnO_2 substrate was needed to get an adequate thickness of 2 mm and immersed in 85% H_3PO_4 for one day, then, heat-treated at 600 °C for 2 h to obtain the composite ceramic. Finally, the resulting ceramic was made into thin disc with the diameter of 15.7 mm and the thickness of 1.49 mm to serve as electrolyte for the electrochemical determinations.

The composite ceramic was ground into powder after polishing the ceramic surface, then, the crystalline structure was determined at room temperature by X-ray diffraction (XRD) analysis. The microstructure of the composite ceramic was observed by a scanning electron microscope (SEM). Platinum paste was coated on both sides (area: 0.5 cm²) of the composite ceramic and heated at 300 °C for 30 min. The composite ceramic was connected to Pt wires and sealed between two alumina tubes, and then placed into an electric furnace for electrochemical measurements. The H_2 /air fuel cell using the composite ceramic as electrolyte and porous platinum as cathode and anode was constructed. The air and H_2 supplied to the fuel cell were unhumidified (water vapor concentration in both chambers was ~3 vol%), the gaseous flow rates were all 30 ml min^{−1} and the operating temperatures were from 150 °C to 250 °C. The impedance spectra of the fuel cell at different temperatures under open-circuit conditions were determined by an AC impedance method using electrochemical workstations (Zahner IM6ex). The frequency range for the measurements was 1 Hz–3 MHz and the ac amplitude was 10 mV. The current–voltage curves were measured to evaluate the performance of the fuel cell.

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 showed the XRD pattern of the obtained powder prepared from the polished composite ceramic. After heat-treated at 600 °C

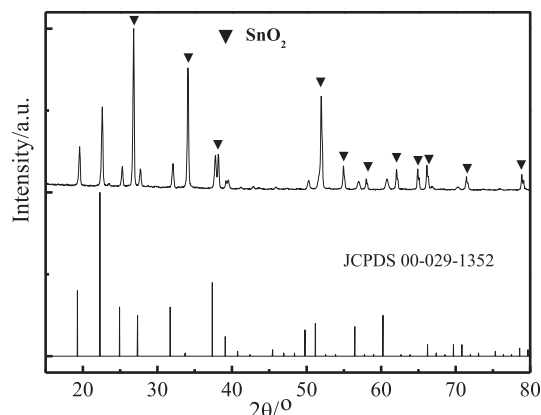
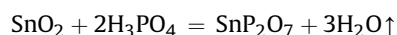


Fig. 1. XRD pattern of the composite ceramic.

for 2 h, the diffraction peaks of SnO_2 (JCPDS 01-077-0452) and SnP_2O_7 (JCPDS 00-029-1352) were observed for the powder. This is because properly concentrated phosphoric acid are favor to form the SnP_2O_7 as indicated by the following equation [30]:



It can be also observed from Fig. 1 that no peak of CuO was detected, suggesting that Cu cations enter in substitutional or interstitial position [29].

3.2. SEM image

The cross-sectional SEM image of the composite ceramic is displayed in Fig. 2. As seen from Fig. 2, the composite ceramic sample is very dense, and the grain is about 4 μm in the mean size. The density of the composite ceramic is 4.15 g cm^{−3}, which is higher than the theoretical density of SnP_2O_7 (3.79 g cm^{−3}) and lower than the theoretical density of SnO_2 (6.92 g cm^{−3}). It is obvious that the variation in the density is attributable to the volume expansion of the ceramic framework caused by the transformation from SnO_2 to SnP_2O_7 [26,27], as confirmed by the XRD result in Fig. 1.

3.3. Performance of H_2 /air fuel cell

Fig. 3 exhibits the impedance spectra of the H_2 /air fuel cell under open circuit conditions in the temperature range of 100–250 °C. The impedance spectra show only one depressed arc which may be ascribed mainly to the interface resistance of electrode–electrolyte. The total cell resistance (R_t), ohmic resistance (R_o) and

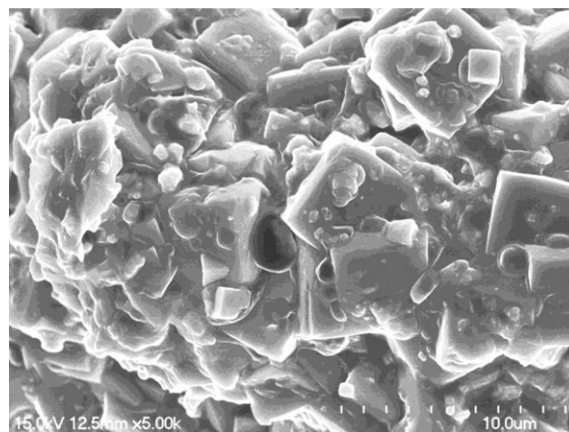


Fig. 2. The cross-sectional SEM image of the composite ceramic.

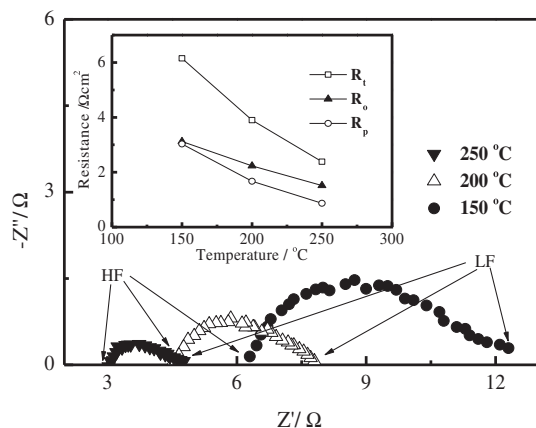


Fig. 3. The impedance spectra of the fuel cell at different temperatures under open-circuit conditions. The total cell resistance (R_t), ohmic resistance (R_o) and interfacial polarization resistance (R_p) as determined from the impedance spectra at different temperatures were shown in the inset.

interfacial polarization resistance (R_p) determined from the impedance spectra at different temperatures are shown in the insert in Fig. 3. The intercepts of the arc with the real axis at low frequency (LF) and high frequency (HF) represent R_t and R_o , respectively, while the difference between R_t and R_o corresponds to R_p [31,32]. The increase of temperature resulted in a remarkable decline of R_p and R_o , typically R_p from $3.03 \Omega \text{ cm}^2$ at 150°C to $0.87 \Omega \text{ cm}^2$ at 250°C and R_o from $3.12 \Omega \text{ cm}^2$ at 150°C to $1.51 \Omega \text{ cm}^2$ at 250°C , respectively. The R_o was always higher than the R_p in the temperature range from 100 to 250°C . The result indicates that under the present conditions R_o is a dominant factor to determine the performance of the H_2/air fuel cell. However, the influence of CuO on the R_t , the R_o and the R_p of the fuel cell based on the $\text{SnP}_2\text{O}_7\text{--SnO}_2$ composite ceramic is unclear yet and the correlative studies are in progress.

The performances of the H_2/air fuel cell are shown in Fig. 4. As seen from Fig. 4, the open circuit voltages are 1.042 V at 150°C , 1.036 V at 200°C and 1.022 V at 250°C , correspondingly. Obviously, they are close to the theoretical values, indicating the composite ceramic electrolyte is sufficiently dense. The peak power densities of the fuel cell reached 39.69 mW cm^{-2} at 150°C , 66.89 mW cm^{-2} at 200°C and 93.71 mW cm^{-2} at 250°C , respectively, which are higher than those of the fuel cells using the electrolyte pellets prepared by merely pressing SnP_2O_7 -based powders [17,18]. This may be owing

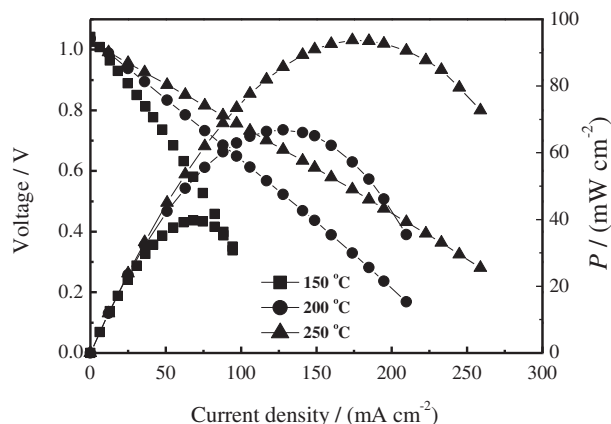


Fig. 4. I – V – P curves for a hydrogen/air fuel cell using the composite ceramic as electrolyte at 100 – 250°C . Electrolyte thickness: 1.49 mm . The air and H_2 supplied to the fuel cell were unhumidified (water vapor concentration in both chambers was $\sim 3 \text{ vol}\%$), the gaseous flow rates were all 30 ml min^{-1} .

to the following reason. The densification is insufficient for the pressed electrolyte pellets. While the Mg-doped $\text{SnP}_2\text{O}_7\text{--SnO}_2$ composite ceramic ($5 \text{ mol}\% \text{ Mg}^{2+}$) has not only a sufficient densification, but also high conductivity related to the restriction for vaporization of phosphorus species during the preparation process at lower sintering temperature (600°C). Thereby, the fuel cell in this study has higher cell performances. The method adopted in this study may be also used to prepare dense $\text{ZrP}_2\text{O}_7\text{--ZrO}_2$ and $\text{TiP}_2\text{O}_7\text{--TiO}_2$ etc. composite ceramic electrolyte fuel cells.

4. Conclusions

In this study, a novel dense Mg^{2+} -doped $\text{SnP}_2\text{O}_7\text{--SnO}_2$ composite ceramic ($5 \text{ mol}\% \text{ Mg}^{2+}$) was prepared by reaction of concentrated phosphoric acid with porous Mg-doped SnO_2 using $1.5 \text{ mol}\% \text{ CuO}$ as a sintering aid at lower temperature (600°C). The result of SEM image indicated that the composite ceramic is very dense. The ohmic resistance (R_o) and interfacial polarization resistance (R_p) was $1.51 \Omega \text{ cm}^2$ and $0.87 \Omega \text{ cm}^2$ at 250°C , correspondingly. The H_2/air fuel cell generated the maximum power densities of 39.69 mW cm^{-2} at 150°C , 66.89 mW cm^{-2} at 200°C and 93.71 mW cm^{-2} at 250°C , respectively. The cell performance may be further improved by decreasing thickness of $\text{SnP}_2\text{O}_7\text{--SnO}_2$ based composite ceramics.

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